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Pilot-Scale Subcritical Water Remediation of Polycyclic Aromatic Hydrocarbon- and Pesticide-Contaminated Soil

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Subcritical water (hot water under enough pressure to maintain the liquid state) was used to remove polycyclic aromatic hydrocarbons (PAHs) and pesticides from highly contaminated soils. Laboratory-scale (8 g of soil) experiments were used to determine conditions for the pilot-scale (8 kg of soil) extractions. Pilot-scale remediations of a PAH-contaminated manufactured gas plant soil (2200 ppm total PAHs ranging from naphthalene to benzo[*ghi*]perylene) with 275 °C water reduced all low and high molecular weight PAHs to below detectable levels (<0.5 ppm) in as little as 35 min. In contrast, removals of higher molecular weight (mutagenic) PAHs were much poorer with either bioremediation for 1 year or supercritical carbon dioxide extraction. Subcritical water extraction at 250 °C of 8 kg of soil contaminated with 70−400 mg/kg levels each of trifluralin, atrazine, cyanazine, pendimethalin, alachlor, and metolachlor also removed all pesticides to below detection limits. While neither the PAH- or pesticide-contaminated soils could support plant growth before extraction, both soils were fertile without additional treatment after extraction (based on germination of lettuce, radishes, and corn); and earthworm toxicity was reduced from 100% to 0%.

Introduction

The majority of the Superfund sites treated between 1982 and 1995 used conventional remediation techniques (*1*) such as soil vapor extraction or vapor stripping for volatile organics (VOC) (*2*−*4*) and incineration or solidification/stabilization for treating recalcitrant pollutants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbon (PAHs), and pesticides (*5*−*8*). Public concern about air emissions and the high cost of incineration has led to the development of alternate technologies for the most recalcitrant organics including soil washing (which uses physical and chemical extraction), electrochemical remediation, and thermal desorption (*9*−*14*). In the last 2 decades, two technologies have received growing interest. Bioremediation, the use of living organisms (primarily microorganisms), has been applied for the remediation of PAHs from manufactured gas plant (MGP) sites, explosives such as TNT, and PCBs from soil (*15*−*29*). Unfortunately, even though bioremediation is one of the most cost-effective technologies, removals of PAHs (especially higher molecular weight species) are frequently poor (*30*−*33*).

Supercritical fluid extraction (SFE) is also a technology that has been successful at cleaning organic-contaminated soils (*34*−*35*). CO_2 is the most common fluid used for SFE, and several bench- and pilot-scale studies have been developed (*36*−*41*) showing removal of PAHs, PCBs, and pesticides. Water appears to be another acceptable solvent, but approaches to using it to remove organic pollutants from historically contaminated soils have generally required the addition of surfactants (*42*), especially for hydrophobic organics (e.g., PAHs, PCBs, and many pesticides) because their solubilities in pure water are too low to allow significant removal to occur. Some attempts to use supercritical water (temperature > 374 °C and pressure> 221 bar) for extracting hydrophobic compounds from environmental solids showed good removals (*43*−*44*). Unfortunately, supercritical water requires temperatures > 374 °C and pressures > 221 bar and is corrosive (*45*), making its use difficult at large scale. Even though water is too polar at ambient conditions to effectively solvate nonpolar pollutants, heating the water to 200−250 °C at 50 bar (enough pressure to maintain the water in liquid state) reduces its polarity (as defined by the dielectric constant, ϵ) to values similar to common organic solvents such as methanol or acetonitrile (*46*). Recently, it has been demonstrated that the drop in water's polarity at so-called "subcritical" conditions (between 100 °C and its critical temperature of 374 °C, with enough applied pressure to maintain the liquid state) dramatically enhances the solubilities of hydrophobic organics. For example, the solubility of anthracene in water increases from 0.08 μg/mL at 25 °C to 2100 μg/mL at 200 °C (a 26 000-fold enhancement), and the solubility of benzo[*a*]pyrene increases from 0.004 μg/mL (at 25 °C) to 1100 μg/mL (at 250 °C), a factor of ∼280 000 (*47*, *48*). Similarly, when the temperature of water is raised from 25 to 200 °C, the solubility of the pesticide propazine increases from 6 to 27000 μg/mL, while chlorothalonil increases from 0.2 to 23 000 μg/mL (*47*).

In addition to the drop in water's polarity which occurs with heating, both the viscosity and surface tension of water are substantially reduced to values similar to or below pure methanol and pure acetonitrile. These factors, along with the increase in organic solubilities, have been used to perform the extraction of PAHs, PCBs, and more polar solutes from a variety of soils and sediments on the analytical (gram) scale (*43*, *49*−*51*). Quantitative removal of PAHs and PCBs from gram samples can be achieved using temperatures ranging from 250 to 300 °C and a 1 mL/min water flow rate (*43*, *51*). While both pressure and temperature can greatly affect the extraction of organics in supercritical CO_2 (*41*), pressure has little effect on the solvent strength of subcritical water as long as the liquid state is maintained (*43*, *51*).

The specific goals of this paper are as follows: (a) to describe the subcritical water extraction laboratory- and pilot-scale systems, (b) to report the feasibility of using subcritical water to remove high concentrations of PAHs and pesticides from two historically contaminated soils, (c) to investigate the effects of the parameters influencing the extraction (temperature, flow rate, and time), and (d) to compare the removals achieved with competitive technologies, including bioremediation and supercritical CO_2 extraction.

Methods

Soil Samples. Two historically contaminated (not spiked) soils were used for the lab-scale and pilot-scale extractions. The PAH-contaminated soil (∼30 kg) was collected at a former

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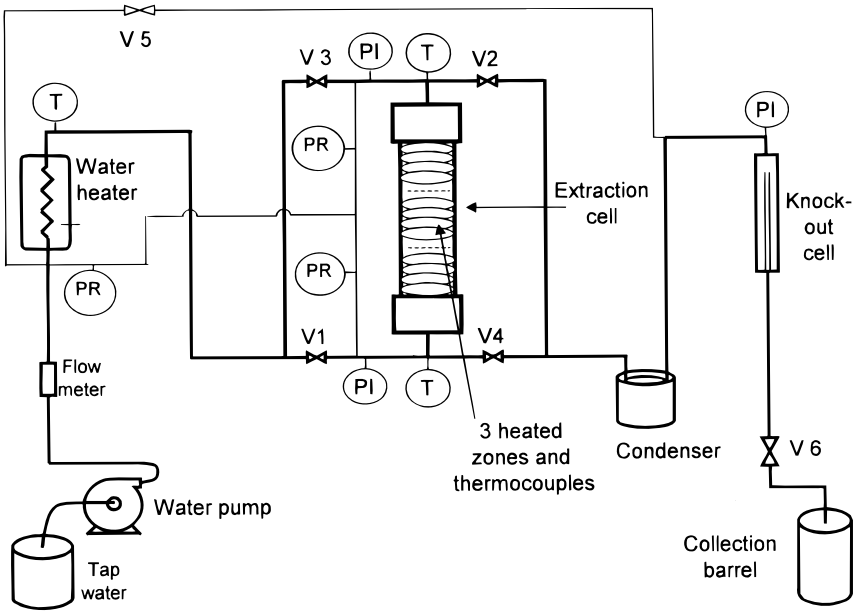

FIGURE 1. Portable pilot-scale (8 kg) remediation unit: V1 to V6: valves, PI: pressure indicator, T: thermocouple, and PR: pressure relief valve.

manufactured gas plant (MGP) ~60 days after the site was opened for bioremediation. Approximately 20 kg of the pesticide-contaminated soil was obtained from a tank loading area. Both soils were sieved (6 × 6 mm mesh screen) to break soil clumps and to remove rocks and were then mechanically mixed to ensure homogeneity. After the initial sieving to <6 mm of the PAH contaminated soil, about 37% was sand particles (from fine to coarse: 6 mm-0.074 mm), 40% was silt (0.074−0.005 mm), 4% was clay (0.005−0.001 mm), and 19% of the particles were smaller than 1 μm (colloids). Based on thermal gravimetric analysis, the moisture content of the PAH- and pesticide-contaminated soils were 11.5 and 8.3 wt %, respectively, and the organic matter contents were 5.2 and 7.0 wt %, respectively.

All soil extracts (after triplicate 18-h Soxhlet extractions with 50:50 methylene chloride/acetone) were analyzed by gas chromatography with flame ionization detection (GC/FID, Hewlett-Packard model 5890 Series II) and gas chromatography/mass spectrometry (GC/MS, Hewlett-Packard model 5972) using a 30-m HP-5 column (0.32 mm i.d., 0.17 μm film thickness). Quantitations were based on calibration standards prepared from stocks of the reported compounds. Total PAHs were based on the total FID response of the PAH extracts compared to the average response factor of the PAH standards.

Subcritical Water Extractions

Laboratory-Scale System. All laboratory-scale extractions were performed using a homemade apparatus previously described (*47*). An Isco model 260D (ISCO, Lincoln, NE) syringe pump was used in the constant flow mode to pump water (HPLC-grade water, Fisher Scientific, Fair Lawn, NJ) through a 1.5-m preheating coil of 1.6 mm o.d. × 762 μm-id (1/16-in. × 0.03 in.) stainless steel tubing, followed by a 6.94 mL extraction cell (9.4 mm i.d. × 100 mm long, Keystone Scientific, Bellefonte, PA) which had been previously filled with about 8 g of soil and vertically mounted in the GC oven (Hewlett-Packard 5890 series II gas chromatograph). Two layers of glass microfiber filter (Whatman Springfield Mill, Maidstone, Kent, U.K.) were placed at the inlet and outlet of the cell. For collection of the extracted organics (so that the organics could be analyzed directly by GC), 0.3 mL/min of toluene ("Optima" grade, Fisher Scientific, Fair Lawn, NJ) was introduced with a second pump (Isco model 100D) into a stainless steel "tee" fitting placed in the oven at the outlet of the extraction cell. The water/analyte/toluene mixture was then cooled in the ice bath using a 1.5-m coil of stainless steel tubing and transferred to the collection vial. This arrangement allows the extracted analytes to partition into the toluene in the heated zone and prevents deposition of the analytes upon cooling. Shut-off valves (HIP Model 15-11AF1-316 from High-Pressure Equipment Co. Erie, PA) were at the pump outlets and extraction system outlet. For safety, a pressure relief valve (Nupro SS-4R3A5, Eden Prairie, MN) was mounted just before the heating coil and vented into a laboratory hood. In addition, both pumps were equipped by the manufacturer with a pressure limit switch set to stop the pump if pressure exceeded a preset value (typically 120 bar in these studies).

To perform an extraction, the toluene valve is closed, while the outlet and the water supply valves are opened. Water is pumped through the preheating coil at a low flow rate (0.1 mL/min) to fill the cell from bottom to top. The system outlet valve is then closed, the pressure is allowed to build to 50 bar (for extractions at 250 °C and below) or 100 bar (for the extractions at 275 °C), and the oven is heated to the desired temperature. The flow is maintained by the pump at a constant 0.1 mL/min until the desired temperature is reached in the oven, and the system pressure is controlled manually at the outlet valve. After the oven reaches its desired temperature, the water flow is increased to the desired value (0.5 or 1 mL/min), the toluene flow is initiated, and the toluene outlet valve is opened after the toluene pump pressure reaches the same pressure as the water pump (pressurization requires only a few seconds). The mixed water/analyte/toluene stream then exits through the cooling coil and is collected in 20 mL glass vials. Throughout the extractions, both the water and toluene pumps are operated in the constant flow mode, and the system pressure is maintained (typically within 5 bar of the desired pressure) by manual adjustments of the system outlet valve. After the water extractions are complete, any pollutants remaining in the soil are determined by extracting the residue for 18 h with 50/50 methylene chloride/acetone.

Pilot-Scale System. The pilot-scale unit was built to scale-up the laboratory unit by about a factor of 1000 (Figure 1), increasing the amount of soil from 8 g to 8 kg. All components

were designed and/or selected based on initial laboratory-scale experiments (discussed below) to determine the influence of water temperature, flow rate, and time on the removal of the PAHs and pesticides. Thus, the pilot-scale unit is designed to operate at temperatures ranging from 100 to 300 °C, at a maximum pressure of 105 bar, and at water flow rates from 0.1 to 1 L/min.

The pilot-scale unit is analogous to the laboratory-scale unit except for the following changes: (1) the water is heated by a propane heater and the extraction cell is heated by thermocouple-controlled heat tapes rather than by an oven as for the laboratory-scale unit and (2) no organic solvent is added to the effluent stream. Instead, the effluent water is cooled and passed through a "knock-out" cell and finally to a wastewater collection barrel. During operation, ambient tap water is pumped by a Hydra Cell model F22/G pump (Wanner Engineering Inc., Minneapolis, MN) through a 30 m heating coil of 6.35 o.d. × 5.31 mm i.d. (1/4-in. × 0.21-in.), stainless steel tubing (used for all connecting lines in the pilot-scale unit) placed directly in the flames of a propane "Master TC 275J Adjustable" heater (purchased at a local hardware store) with adjustable output up to 58 600 W (200 000 Btu/h). Water outlet temperature from this arrangement is manually controlled to ∼ ± 5 °C (based on a thermocouple placed in the heater outlet line) by adjusting the burner flame. Water then passes into the 8.2-L tubular extraction cell (10.2 cm i.d., 12.7 cm o.d. × 100 cm long [4″ × 5″ × 40″], High-Pressure Equipment, Erie, PA) which includes stainless steel frits (0.5 μm pore size) at the inlet and outlet ends. Additional heat is provided to the extraction cell via six heat tapes (bottom, middle, and top, 620 W each) all under separate thermocouple control. After passing through the cell from bottom to top, the water passes through a 30-m cooling coil placed in the barrel of water, then through a "knock-out" cell (4.9 cm i.d. × 6.0 cm o.d. × 100 cm long stainless steel tube), and finally to a wastewater collection barrel. (Note that the system was designed so that the water flow can be reversed to top to bottom to regain flow if plugging occurs or for applications where top to bottom flow is desired). As for the laboratory-scale system, a constant water flow rate is set at the pump, and the system pressure is controlled by a manual valve (ss 10-11AF4, High-Pressure Equipment Co, Erie, PA; the same valve style was used at all locations shown in Figure 1) and at the outlet of the system (Figure 1). Pressure relief valves (Nupro ss 177-R3A-K1-D (103−155 bar), Willoughby, OH) were placed in multiple positions throughout the extraction system so that no part of the unit could be isolated from a pressure relief valve regardless of the status of the control valves.

Problems that occurred during the initial shake-down experiments conducted with uncontaminated soil were related to plugging the outlet frit with fine soil particles or swelling of the soil (upon pressurization with the water) causing it to expand to completely fill the cell and form an impermeable mass. Plugging based on the expansion of the soil was simply solved by leaving ∼15 cm headspace at the top of the cell. Plugging of the outlet frit with fine soil particles occurred when the extraction cell was filled with room temperature water and the entire system was pressurized prior to turning on the gas and electric heaters, apparently because of fluidization and transport of fine particles to the outlet (top) frit. However, by first filling the soil column with room temperature water and then preheating the water and the soil before beginning the extractant water flow (as described below), none of the subsequent extractions (12 individual runs of contaminated and uncontaminated soils) experienced even slight plugging, and a maximum of only ∼4 bar pressure drop was observed between the inlet and outlet of the 8-L cell.

The final procedure used to perform the experiments at the pilot scale is similar to the laboratory procedure. About 8 kg of soil was loaded in the extraction cell (leaving 15 cm headspace at the top). Tap water was pumped from the bottom to the top of the opened reactor at ∼570 mL/min until water started to fill the headspace. The outlet of the reactor was then capped, the outlet valve was closed (valve V2 in Figure 1), and the electric heaters mounted on the extraction cell were turned on. After 1 h of preheating (at which time the internal soil temperature was ∼150 °C as determined by thermocouples inserted into the top and bottom radial center of the soil column), the propane heater was lit and the water flow was begun. As with the laboratory-scale system, the water flow rate was controlled by the pump, and the system pressure was controlled by manually adjusting the outlet valve. Effluent wastewater was collected periodically and analyzed after extraction with methylene chloride. After the pilot-scale run was complete, the system was allowed to cool for ∼4 h, and three samples of soil were then collected (bottom, center, and top of the soil column) and analyzed to determine the removal efficiencies.

Supercritical Fluid Extraction. Supercritical fluid extraction (SFE) was performed using an Isco model SFX-210 extractor equipped with coaxially heated restrictors and a model 260D pump. Extraction conditions were based on reports of optimizing SFE for remediation of PAH-contaminated soil (*37*). CO_2 flow rates and soil sample sizes were chosen so that the ratio of CO_2 to soil used was the same as that reported by Montero et al. (*37*). Thus, for extractions at 103 bar, triplicate 2.9-g soil samples were each extracted at ∼0.65 mL/min (condensed CO_2 as measured at the pump), and for the 330 bar extractions triplicate 4.8 g soil samples were extracted at ∼1.4 mL/min. After the CO_2 extractions were complete, the soil residues were extracted in a Soxhlet apparatus with 50/50 methylene chloride/acetone for 18 h, and the percent removals were calculated based on the PAH concentrations remaining in the soils compared to the original concentrations.

Soil Fertility. Approximately 130 g each of the PAH- and pesticide-contaminated soils (before and after the pilot-scale treatment) were placed in clay pots and four seeds each of lettuce, radishes, and corn were planted ∼0.5−1 cm deep in each test soil pot. An uncontaminated soil from a very productive local garden was used as a control. All soils were placed in sunlight in separate trays (to avoid cross-contamination) and watered as needed. Positive germination was defined as a healthy looking seedling which reached a height of >2 cm (∼1−2 weeks after planting).

Results and Discussion

Remediation of the PAH-Contaminated Soil. Initial laboratory-scale extractions of the PAH-contaminated soil (concentrations of individual PAHs range from ∼7 to 100 ppm, Table 1) were performed using 8-g samples with a water flow rate of 0.2−1 mL/min and a temperature ranging from 175 to 275 °C. Fractions of the effluent water were collected every few minutes to allow the extraction profile (percent removal vs time) to be determined for all of the individual PAHs in the soil. The removal efficiency for each test was also verified by determining the concentration of each PAH left on the soil residue (after subcritical water extraction). Mass balance (i.e., the sum of PAHs collected from the extractant water plus any PAHs in the treated soil residue compared to the PAH content in the untreated soil) agreed within the analytical reproducibility for PAH determinations (typically ±10%).

At the lower temperatures (175 and 200 °C), only the lower molecular weight PAHs were efficiently removed from 8 g of soil, while the removal of the higher molecular weight PAHs was poorer. For example, after 2 h of extraction at 200 °C (1 mL/min), >99% of the naphthalene and acenaphthene were

TABLE 1. Pilot-Scale (8 kg) Removal of PAHs from an MGP Soil Treated with Subcritical Water at 275 °C

		concn, mg/kg	
	MW	untreated soil (% RSD)[a]	treated soil[b,c]
naphthalene	128	6.6 (2)	<0.3
2-methylnaphthalene	142	9.5 (2)	<0.3
1-methylnaphthalene	142	14 (1)	<0.3
acenaphthene	154	46 (3)	<0.4
fluorene	166	18 (2)	<0.3
phenanthrene	178	52 (6)	<0.3
anthracene	178	34 (1)	<0.5
fluoranthene	202	53 (5)	<0.3
pyrene	202	100 (4)	<0.3
benz[*a*]anthracene	228	44 (5)	<0.3
chrysene	228	49 (5)	<0.3
benzo[*b*+*k*]fluoranthene	252	84 (2)	<0.4
benzo[*e*]pyrene	252	45 (2)	<0.4
benzo[*a*]pyrene	252	54 (1)	<0.4
indeno[1,2,3-*cd*]pyrene	276	31 (5)	<0.5
benzo[*ghi*]perylene	276	39 (8)	<0.5
sum of identified PAHs[d]		680 (2)	
total concn[e]		2200 (2)	

[a] Concentrations on the untreated soil based on triplicate 18-h Soxhlet extractions. [b] All three pilot runs showed concentrations for each compound below detection limit. Soxhlet extractions of the residue from the top, middle, and bottom of the reactor were performed for each pilot run. [c] Duplicate pilot runs were performed at 275 °C, 100 bar, 300 mL/min for 2 h and a single run at 275 °C, 100 bar, 600 mL/min for 1 h. [d] Sum of individual PAHs listed in the table. [e] Total PAH concentration based on the total GC/FID peak areas.

removed, but the removal of PAHs with higher molecular weights was only ~60%, 30%, and 15% for PAHs having molecular weights of 228, 252, and 276, respectively. Extraction rates at 0.2 mL/min were ~5-fold slower than those at 1 mL/min (i.e., plots of percent removal versus water volume are nearly identical for the two flow rates for all of the PAHs), indicating that the extraction efficiency depends mostly on water volume rather than contact time over the range of flow rates studied.

When the extraction temperature was raised to 250 °C and the flow rate was 1 mL/min, removal of all of the PAHs except those with molecular weights of 252 and 276 was >99% after 60 min. Finally, at 275 °C, all PAHs were removed to below the detection limit (~0.5 ppm) in the soil residue in less than 40 min. Similar extraction behavior has been observed for PAHs from different soils and matrices including air particulate matter, waste sludge, and contaminated catalysts (*43, 50*), indicating that PAH extractions are not likely to be greatly affected by different soil types. Since the water heating unit in the pilot-scale system was capable of heating 0.5−0.6 L/min of water to 275 °C, the removal rate of PAHs at 275 °C was determined using the laboratory system at 0.5 mL/min (the same water-to-soil ratio as using 0.5 L/min for an 8-kg pilot-scale run). Under these conditions, 60 min was sufficient to remove all of the PAHs from the 8-g sample, and extraction of the soil residue demonstrated that all PAHs (ranging in molecular weight from 128 to 276) were removed to below the analytical detection limit (~0.5 ppm).

Based on the laboratory-scale results, three pilot-scale extractions of the same PAH-contaminated soil were performed, all at 275 °C (100 bar). First, duplicate extractions of 8-kg soil samples were performed at a water flow rate of 300 mL/min for 2 h (~9 pore volumes). As shown in Figure 2, the extraction of the various PAHs shows the expected pattern, i.e., the lower molecular weight PAHs extract at the fastest rate, while the higher molecular weight PAHs require longer extraction times. Note also that the initial appearance of the higher molecular weight PAHs is delayed by up to 20 min (while the appearance of these PAHs is not delayed in the laboratory-scale extractions). The delay in appearance in the higher molecular weight PAHs is likely a result of the slower soil heating which occurs in the pilot-scale unit. As discussed below, the soil temperature upon starting the extraction was only ~150 °C, and ~30 min is required for the top (outlet end) of the soil to reach 275 °C. Despite the delay in the extraction rate of the higher molecular weight PAHs, both of the duplicate pilot-scale runs at 300 mL/min showed similar extraction curves, and complete removal of the PAHs was achieved in ~60−70 min, which corresponds to a water volume of ~21 L (~5 pore volumes).

No detectable PAHs (<0.3−0.5 ppm) were found in the three subsamples (bottom, middle and top of the soil column) collected from the 8-kg samples after the 2-h extractions with 300 mL/min of 275 °C water, as shown in Table 1. The total PAH concentration was reduced from the initial 2200 ppm to nondetectable levels.

The third pilot-scale run was also performed at 275 °C (100 bar), but the water flow rate was doubled (to 600 mL/min) and the extraction time was cut to 1 h. The removal of PAHs after 1 h was the same as those shown in Table 1, i.e., no PAHs could be detected in the soil. The extraction was completed after 35−40 min, which also corresponds to ~21 L of water, as was the case for the 300 mL/min runs (Figure 2). Thus, based on the results discussed above, the time required for complete removal of the PAHs can be reduced (without increasing the amount of water required) by increasing the water flow rate, at least up to 600 mL/min for 8 kg of soil.

As discussed above, the pilot-scale extraction cell was heated after filling with soil and water with heat tapes for 1 h before beginning the flow of hot (250−275 °C) extractant water. The major difference between the laboratory-scale and pilot-scale units is the heating rate of the soil column. For example, when an extraction temperature of 250 °C is used with the laboratory system, the water temperature at the outlet of the cell is ~240 °C in less than 2 min after the water flow is started. In contrast, heating the soil column in the pilot-scale reactor is relatively slow. When only the heat tapes are used to heat the soil column, the temperature of the soil increases in a nearly linear fashion (monitored with thermocouples inserted into the center of the soil column ~15 cm from the top and bottom of soil) but requires ~2 h to approach the set-point temperature. For example, when the set point is 275 °C, the soil temperature (top and bottom) is ~150 °C after 60 min.

Since 1 h of preheating was experimentally convenient, the propane heater and water pump were started after 1 h so that the hot extractant water could supply heat to the soil column and, therefore, reduce the total time required for the process. This procedure was followed by all pilot-scale runs. Although the inlet water temperature jumped to within 10 °C of the set-point temperature in only ~2 min, heating of the soil is naturally slower. For example, when the inlet water temperature was set at 275 °C and the water flow rate was ~300 mL/min, the temperature of the soil inside the cell at the bottom (inlet) required ~7 min to reach 240 °C and ~12 min to reach 275 °C. The temperature of the soil at the top was 240 °C after 20 min of hot water flow and 275 °C after 30 min. However, as demonstrated by the extraction results for the PAH- and pesticide-contaminated soils, heating of the soil (and extractant water) by this approach was sufficient to perform the desired removal of the pollutant organics.

It should be noted that, as the water cools before wastewater collection in the pilot-scale unit, PAHs could potentially drop out of solution. As shown in Figure 1, a "knock-out" cell was installed to allow any phase-separated material to be collected. Analysis of the wastewater collected from the pilot-scale runs showed that virtually all of the lower

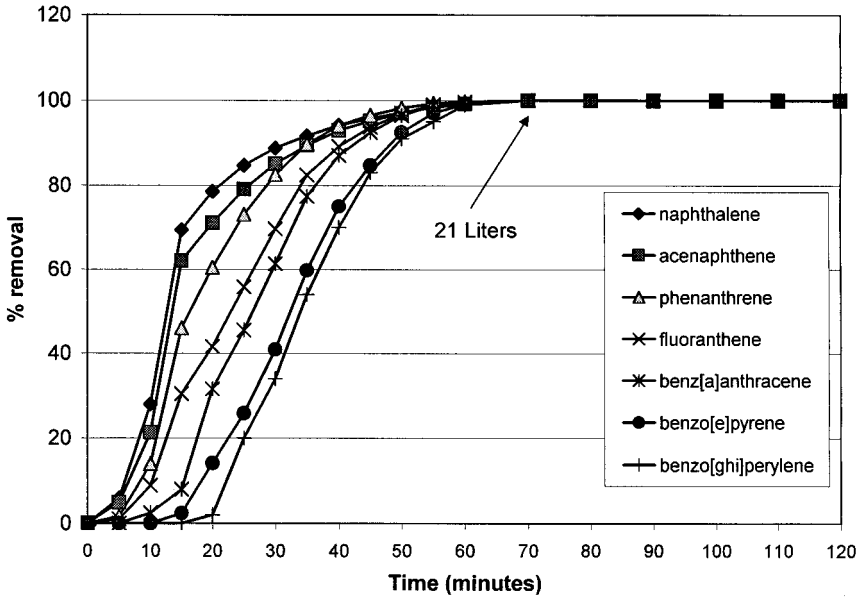

FIGURE 2. Subcritical water extraction of PAHs from 8 kg of soil at 300 mL/min, 275 °C, for 120 min.

molecular weight (the most water soluble) PAHs were found in the wastewater and did not precipitate prior to the wastewater collection barrel. In contrast, approximately 20−40% of the total extracted mass of the highest molecular weight PAHs (which are the least water-soluble PAHs) were found in the wastewater barrel. These results were somewhat surprising since the concentrations of all of the individual PAHs with molecular weights of 178 and greater (i.e., phenanthrene and larger PAHs) in the wastewater collection barrel were considerably higher than their water solubilities at 25 °C.

Interestingly, the wastewater was very brown and foamy and apparently contained large amounts (about 50% of the initial concentration in the soil) of coextracted soil organic material (e.g., several phenols and nitrogen-containing organics consistent with humic acid pyrolysis were identified by GC/MS in extracts of the wastewater). Upon standing overnight, large amounts of flocculated material formed at the bottom of the wastewater barrel. Additional wastewater samples were taken from the barrel which did not contain the flocculated material and analyzed as before. While the fresh wastewater contained ppm concentrations of individual PAHs (e.g., ~1, 4, 6, 3, 1, and 2 ppm for naphthalene, phenanthrene, pyrene, benz[*a*]anthracene, benzo[*a*]pyrene, and benzo[*ghi*]perylene, respectively), after standing overnight the supernatant wastewater was almost completely void of the PAHs (i.e., naphthalene was reduced to 0.2 ppm, phenanthrene to 0.02 ppm, and all other PAHs listed above were reduced to less than 0.01 ppm). This water was certainly clean enough to be recycled through the extraction unit to remove PAHs from additional soil. Additional lab studies on fresh wastewater indicated that similar PAH removals by separating the flocculated material from the wastewater could be achieved after only 2 h of settling, thus indicating that water recycling in a commercial unit may be viable.

Remediation of the Pesticide-Contaminated Soil. Initial laboratory-scale extractions were performed on 8-g samples of the pesticide-contaminated soil at 100, 175, and 250 °C (1 mL/min) for a 15-min extraction time. Even 100 °C extractions for 15 min reduced the more water soluble pesticides listed in Table 2 by ~one-half, but trifluralin and pendimethalin showed no removal at 100 °C. Increasing the temperature to 175 °C gave good removals (>99%) of all pesticides except trifluralin and pendimethalin, while extraction with 250 °C efficiently removed (>99%) all of the pesticides in 15 min.

TABLE 2. Laboratory- (8 g) and Pilot-Scale (8 kg) Removal of the Pesticides from a Historically Contaminated Soil Treated with Subcritical Water

	solubility[a] in water (ambient), mg/L	untreated soil, mg/kg (% RSD)	soil treated at pilot scale 1 h,[b] 250 °C mg/kg
trifluralin	<1	100 (1)	<0.1
atrazine	30	187 (3)	<0.1
alachlor	242	73 (8)	<0.1
metolachlor	530	111 (6)	<0.1
cyanazine	171	400 (10)	<0.1
pendimethalin	0.3	415 (2)	<0.1

[a] Solubility of the pesticides at ambient temperature (20−27 °C) from ref *57*. [b] Concentrations of the pesticides left in the soil after subcritical water treatment.

The faster removals with higher temperatures are similar to those discussed above for PAHs and earlier reports for PCBs (*43*, *51*); however, the removal of all of the pesticides is easier to achieve than nearly all of the PAHs (with the possible exception of the lowest molecular weight PAHs) and all PCB congeners. This might be expected since, in general, the solubility of pesticides in ambient water is much higher than individual PAHs and PCB congeners.

Although the laboratory-scale extractions indicated that lower temperatures would be sufficient to treat the pesticide-contaminated soil, the pilot-scale unit was operated at 250 °C to ensure good removals. The extraction of the 8-kg soil sample was performed for 1 h using a 400 mL/min of water, and the effluent water was collected every few minutes to allow the extraction profiles to be determined. As with the PAH-contaminated soil, the filled extraction cell (soil and water) was preheated for 1 h (to ~150 °C) before beginning the flow of the 250 °C extractant water.

As shown in Table 2, the 1-h extraction reduced all of the contaminant pesticides from their initial concentrations (up to 400 ppm) to below detectable levels (<0.1 ppm). The extraction profiles of all of the pesticides showed similar behavior to those shown by PAHs in Figure 2, although the extraction of pesticides was somewhat faster than the PAHs. For pesticides, complete removal was achieved after ~40 min using ~16 L of water for the 8-kg sample.

Soil Productivity. Although extensive toxicity testing was beyond the scope of this study, a simple seed (monocot and dicot) germination test was performed on both the PAH-

TABLE 3. Concentrations on the PAH-Contaminated Soil after 1 Year of Bioremediation

	untreated, mg/kg (% RSD)[a]	bioremediation, mg/kg (% RSD)[a]
naphthalene	48 (3)	8 (5)
2-methylnaphthalene	118 (3)	8 (6)
1-methylnaphthalene	112 (3)	6 (6)
acenaphthene	129 (1)	6 (12)
fluorene	136 (4)	12 (16)
phenanthrene	434 (4)	23 (18)
anthracene	110 (6)	14 (5)
fluoranthene	130 (5)	41 (8)
pyrene	197 (4)	82 (7)
benz[*a*]anthracene	74 (2)	46 (3)
chrysene	77 (4)	51 (3)
benzo[*b*+*k*]fluoranthene	88 (14)	58 (2)
benzo[*e*]pyrene	39 (13)	30 (6)
benzo[*a*]pyrene	50 (11)	43 (5)
indeno[1,2,3-*cd*]pyrene	19 (11)	14 (17)
benzo[*ghi*]perylene	27 (12)	26 (12)
sum of identified PAHs[b]	1788 (4)	468 (2)
total concn[c]	5820 (4)	1840 (4)

[a] Based on triplicate Soxhlet extractions of the soil before and after bioremediation treatment. [b] Sum of individual PAHs listed in the table. [c] Total PAH concentrations based on the total GC/FID peak areas.

and pesticide-contaminated soil before and after the pilot-scale extractions as well as on a "control" soil (a local garden soil). Before treatment, neither the PAH- nor the pesticide-contaminated soil could support germination of radishes, corn, or lettuce. However, after remediation both soils showed germination rates similar to the "control" garden soil, i.e., germination for radish, corn, and lettuce (respectively) was 75, 75, and 50% for garden soil; 75, 75, and 100% for the treated PAH soil, and 50, 50, and 50% for the treated pesticide soil. While these results are only an initial measure of soil productivity, they do demonstrate that subcritical water extraction is likely to be more beneficial for final land reclamation than technologies such as incineration or soil washing with organic solvents or surfactants.

Earthworm Toxicity. A screening-level earthworm toxicity test was performed on both treated and untreated soils by exposing 5 worms (*Eisenia fetida*) to 25 g of soil (at a moisture content of approximately 80% of field capacity) for a 28-day period (*58*). Each test was performed in triplicate. Both the untreated pesticide- and PAH-contaminated soils were shown to be highly toxic with 100% mortality observed within 48 hours. However, no mortality (100% survival) was observed in the treated soils after the 28-day of exposure period.

Comparison to Other Treatments

Bioremediation. Comparison of our subcritical water extractions with bioremediation was possible in the present study since the MGP site which provided the soil used in our extraction studies has also undertaken on-site bioremediation on a several hundred m^3 field unit. The bioremediation process essentially involved placing the contaminated soil in a lined pit and tilling frequently for approximately 1 year. At this time, samples were obtained from four locations on the treatment site, homogenized, and analyzed in the same manner as the soil used for our pilot-scale extractions.

The removal of PAHs from this field bioremediation is summarized in Table 3. While the removal efficiencies of the lower molecular weight PAHs were fairly high, little or no removal of the higher molecular weight PAHs (including the majority of mutagenic PAHs) was achieved, in agreement with earlier reports (*31*−*33*). In contrast, the pilot-scale subcritical water extraction removed all of the PAHs to below ∼0.5 ppm, regardless of their molecular weight (Table 1).

TABLE 4. Supercritical CO_2 Removal of PAHs from an MGP Soil after 200 Min

	concn, mg/kg (% RSD)[a]			
		treated soil		
	untreated soil	103 bar (45 °C)	330 bar (45 °C)	400 bar (150 °C)
naphthalene	6.6 (2)	4.6 (8)	4.0 (25)	<0.5
2-methylnaphthalene	9.5 (2)	1.4 (42)	1.3 (44)	<0.5
1-methylnaphthalene	14 (1)	2.0 (18)	1.9 (16)	<0.5
fluorene	18 (2)	3.6 (14)	3.0 (24)	<0.5
phenanthrene	52 (6)	21 (30)	7.5 (91)	<0.5
anthracene	34 (1)	30 (8)	9.4 (51)	<0.5
fluoranthene	53 (5)	36 (17)	9.4 (44)	<0.5
pyrene	100 (4)	69 (18)	18 (52)	<0.5
benz[*a*]anthracene	44 (5)	32 (11)	11 (20)	3.0 (32)
chrysene	49 (5)	36 (12)	14 (28)	5.1 (34)
benzo[*b*+*k*]fluoranthene	84 (2)	45 (15)	28 (11)	12 (24)
benzo[*e*]pyrene	45 (2)	37 (15)	27 (17)	9.5 (25)
benzo[*a*]pyrene	54 (1)	51 (16)	25 (17)	11 (27)
indeno[1,2,3-*cd*]pyrene	31 (5)	17 (18)	12 (18)	10 (19)
benzo[*ghi*]perylene	39 (8)	26 (21)	17 (23)	14 (20)
sum of identified PAHs[b]	680 (2)	412 (14)	188 (23)	65 (30)
total PAH concn[c]	2200 (2)	1300 (6)	740 (28)	300 (32)

[a] Based on triplicate 18-h Soxhlet extractions performed on the soil before and after the various treatments. [b] Sum of the individual PAHs listed in the table. [c] Total PAH concentrations based on the sum of individual GC/FID peak areas.

Supercritical CO_2. Extraction of PAHs with supercritical CO_2 using the conditions suggested by Montero et al. (*37*) were applied at the laboratory-scale (with flow rates adjusted so that the ratio of CO_2 to soil was the same as in ref *37*) to the same MGP site soil used for our 8-kg subcritical water extractions (Table 1). Extraction with 103 bar CO_2 (45 °C, 200 min) did reduce the total PAH concentration from ∼2200 to 1300 ppm (Table 4), while extraction at 330 bar (45 °C, 200 min) reduced the total PAH concentration to 740 ppm. The extraction of individual PAHs was generally much better at 330 bar than for the 103 bar extractions for all of the higher molecular weight PAHs (phenanthrene and larger). Interestingly, neither pressure resulted in complete removal of the naphthalene, in contrast to the results reported by Montero et al. based on the extraction of spiked naphthalene (*37*). This relative ease in extracting spiked PAHs compared to historically aged PAHs agrees with previous reports for analytical-scale extraction of PAHs from soil using supercritical CO_2 (*52*). Other reports have used supercritical CO_2 for analytical extractions of PAHs at elevated temperatures (150 °C) and pressures (400 bar) and demonstrated increased removal of PAHs over those obtained at lower (e.g., 45 °C) temperatures (*41*, *53*−*55*). Therefore, additional extractions were performed at 400 bar and 150 °C on the MGP soil. Under these conditions, the removal of all of the PAHs was higher, but significant concentrations of PAHs starting with benz[*a*]anthracene and larger remained on the soil, again demonstrating that subcritical water was more effective at removing all molecular weights of PAHs from the soil (Table 4).

While an in-depth economic analysis is beyond the scope of this study, general comparisons can be made with other approaches. Estimates reported by Montero et al. (which include operational costs for treatment, but exclude any operational costs on capital) (*37*), set the cost per m^3 of treating PAH-contaminated soil using supercritical CO_2 at $170 to $200, supercritical water oxidation at $250 to $733, methanol extraction at $400 to $514, bioremediation at $190 to $370, and incineration at ∼$1600 per m^3. Using the same assumptions as Montero applied to subcritical water extraction, we obtained a cost of $150 per m^3 for the conditions which were successful in treating the PAH-contaminated soil

(Table 1). For comparison, an independent engineer using our subcritical water conditions, the 330 bar and 45 °C conditions of Montero, and process simulation software which includes all related capital, maintenance, operational, and process-related disposal costs (ASPEN Plus, release 9, Aspen Technology, Inc., Cambridge, Massachusetts, USA), estimated a final cost of $490 per m^3 for supercritical CO_2 and $220 per m^3 for subcritical water.

While the preliminary economic evaluations described above can only be used for relative comparisons among different technologies, the relatively favorable costs for subcritical water and the high removals achieved in our study for PAHs and pesticides support the continued development of subcritical water extraction for other organic pollutants and future determinations of its optimal design, application, and cost (*56*).

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